

(19) Japanese Patent Office (JP)

(12) **Kokai Unexamined Patent Application Bulletin (A)**

| | | |
|------|---|---------------|
| (11) | Laid Open Patent Application No. | 64-63039 |
| (43) | Publication Date | March 9, 1989 |
| | Number of Inventors | 1 |
| | Number of Pages | 7 |
| | Examination Request | Not yet made |

| (51) | Int. Cl. ⁴ | Identification Code | Internal File No. |
|------|-----------------------|---------------------|-------------------|
| | B 01 J 20/30 | | 6939-4G |
| | A 23 L 3/34 | 301 | 7329-4B |
| | B 01 J 20/02 | | 6939-4G |

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| (54) | Title of the Invention: | Method for producing deoxygenation agent |
| (21) | Application No.: | 62-216527 |
| (22) | Application Date: | September 1, 1987 |
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SPECIFICATION

1. Title of the Invention

Method for producing deoxygenation agent

2. Claims

A method for producing a deoxygenation agent, characterized in that micropowdered metal halide is finely mixed and affixed to metal powder surfaces by means of carrying out simultaneous milling and mixing of the metal halide and the metal powder with a water content of 1% or less.

**3. Detailed Description of the Invention
(Field of Industrial Application)**

The present invention relates to a deoxygenation agent that is used for storage and preservation of foodstuffs.

(Prior Art)

In order to prevent spoiling and mold growth during storage of foodstuffs including vegetables and fish, vacuum packing methods, cold storage methods and gas purge methods have been used in the past. However, these methods have the disadvantage of requiring costly equipment and a fairly high level of technology for their implementation.

In terms of methods for solving this problem, various proposals have been made and implemented in regard to deoxygenation agents that employ the principle whereby iron powder reacts with and fixes atmospheric oxygen in the presence of water.

In particular, JP-56-033980-B proposes a method

for producing an oxygen absorption agent formed by coating a metal powder with a metal halide, the amount of metal halide for coating being 0.001 to 5 parts with respect to 100 parts of metal powder; a solution of the metal halide is mixed with the metal powder and an oxygen absorption agent having a total water content of 1% or less with respect to the entire weight, thereby bringing about coating with the metal halide, whereupon drying is carried out until the water content is 1 wt% or less.

In addition, JP-60-020986-A proposes a deoxygenation agent produced by uniformly mixing an electrolytic micropowder, no less than 50 wt% of which passes a 150 mesh with an iron powder, no less than 50 wt% of which passes a 150 mesh.

However, these deoxygenation agents produced by these conventional technologies present the following problems. JP-56-033980-B is characterized in that the surface of the metal is coated with the metal halide. For this reason, it is necessary to dissolve the metal halide in water, alcohol or other liquid and to treat the metal powder with this liquid.

Specifically, it is necessary to carry out a complicated operation whereby the solution and metal powder are mixed and then dried. In this case, drying must be carried out by rapid drying under vacuum or reduced pressure in order to prevent oxidation of the metal powder, and thus the size of the equipment increases, which means that the product is expensive. Moreover, because the metal halide is used in the form of a solution, problems such as the treatment of waste liquid arise, and thus the method cannot be considered to be satisfactory.

In contrast, the deoxygenation agent described in JP-60-020986-A does not require a solution preparation step or a drying step as with the former JP-56-033980-B, but there are parameters placed on the iron powder and electrolytic powder that are used.

It is necessary to adjust the amounts thereof that pass a 150 mesh to 50 wt% or greater prior to mixing, and thus there is the disadvantage that a sieving step is required. Moreover, there are also particle size ranges for the iron powder and electrolytic powder, and in order to obtain a material of which no less than 50% passes a 150 mesh, sieving alone does not suffice to achieve a balance, meaning that it is necessary to mill the coarse particles.

In addition, there are problems with product reliability because a close physical relationship between the iron powder and metal halide is not necessarily produced by means of simple mixing.

(Problems to Be Solved by the Invention)

The present invention, as described above, is a method for producing a deoxygenation agent that solves production problems such as the necessity of dewatering treatments, difficulties with adjusting starting materials, and the need for costly equipment, which arise when attempting to produce deoxygenation agents using conventional technologies.

(Means for Solving the Problems)

When an aqueous solution of a metal halide and iron are present together, it is well known that iron undergoes corrosion, which is to say oxidation, to a greater extent than when exposed to ordinary environments. This is because the metal halide is ionized, facilitating electron transport in the oxidation.

In addition, even with metal halides that are in a dry state, it is also known that most have deliquescent properties, so deliquescence occurs due to the water content present in the atmosphere, and oxidation progresses in a similar manner. This also occurs by means of the mechanism described above.

In order to produce a deoxygenation agent having stable performance that employs iron and metal halide, it is necessary for a condition to be produced wherein suitable amounts of the metal halide and the iron powder are mixed closely and homogeneously, and preferably so as to produce close adherence at the metal surface.

However, if a condition is to be reached in which this coating has occurred, then it is necessary to use costly equipment of the type described above and to

carry out complicated procedures. In addition, with simple mixing, it is necessary for the raw materials to adhere to strict parameters, [and thus] a stable product cannot be obtained.

Thus, as a result of various repeated investigations, it was found that a desirable state is obtained for the metal powder and metal halide by combining the metal powder and metal halide, introducing them into a mill, preferably a rod mill or ball mill, and carrying out simultaneous milling. That is to say, when these are simultaneously milled, the brittle metal halide is milled to a greater extent, thus producing a finer material than the metal powder.

Consequently, as a result of the ball or rod grinding action and the particle diameter differential between the two, the metal halide powder is affixed to the surfaces of the metal powder that is coarser than the metal halide. In addition, this is firmly affixed because new interfaces are exposed as a result of milling of the metal halide and metal powder.

In addition, it was found that, because mixing is carried out simultaneous to milling, the metal halide is not sedimented to a greater extent [than the metal powder], and a metal halide treated iron powder having uniform and stable deoxygenation capacity can be obtained.

(Operation)

The present invention is based on this knowledge, and solves the problems of equipment cost and process complexity that were conventionally required in the production of deoxygenation agents, making it easy to produce a deoxygenation agent having stable performance.

Fig. 1 shows a production process for the deoxygenation agent of the present invention.

The particle size of the metal powder used in the present invention may be coarse or fine, and by setting the milling conditions appropriately, a deoxygenation agent can be produced that has the desired particle size. Consequently, it can be said that there are substantially no [required] parameters for the metal powder.

The metal powder raw material is a material that is produced, for example, by preliminary crushing to generate multiple fissures in particulate iron generated during iron production or dry iron generated during mechanical processing of cast iron, and even if brittle manufactured electrolytic iron is used, an iron powder can be obtained that has

similar deoxygenation capacities as when metal powder is used.

In particular, when a metal halide that is extremely deliquescent is used, there is the problem of a moderate degree of bleeding into the packaging material that encloses the deoxygenation agent, but when dry powder or cast iron powder that comprises graphite in the metal powder is used, characteristics are obtained whereby bleeding is reduced, and the cast iron powder treated with metal halide is not tacky, which facilitates handling. This is thought to be because the graphite in the cast iron powder serves to adjust water content and also serves as a retaining material for the metal halide.

In addition, the material that is used for the metal powder is not limited to iron, as any metal that oxidizes in air may be used. However, iron is the most preferred because it is inexpensive, readily procured, and stable in powder form.

Various types of metal halides may be cited as the metal halide that is used together with the above mentioned metal component. Examples include halides of alkali metals such as NaCl, KCl, NaBr and KBr, halides of alkaline earth metals such as NaCl, CaCl, CaBr₂, MgBr₂ and BaBr₂, as well as halides of various metals such as AgCl, ZnCl, AlCl₃, SnCl, MnCl, FeCl₃, CoCl₂, NiCl₂, ZnBr₂, SnBr₂, CuBr and FeBr₂.

These may be used individually or mixtures may be appropriately selected when actually used. Of course, the metal halide may be a powder, granules, or clumps. It may be said that almost any mode may be used for the present invention.

From the results shown in Fig. 2, there are no particular restrictions on the amount of metal halide used in the present invention, but the amount as converted to anhydride is 0.01 to 10 parts by weight, and preferably 0.5 to 5 parts by weight, with respect to 100 parts by weight of metal powder component.

If the amount of metal halide used is too low, at 0.01 parts by weight or less, then the effects will be insufficient and the initiation time for the deoxygenation agent will increase. It is, of course, not economical for the amount to be too high, at 10 parts by weight or greater, and generation of hydrogen gas or bleeding of the content due to deliquescence of the metal halide will also result. Consequently, the amount of metal halide used in the present invention should be in the range of 0.5 to 5 parts by weight.

Production of the deoxygenation agent according to the present invention is carried out in the manner described below.

The metal powder and metal halide described above are first dried to produce a water content of 1% or less. This drying may be omitted with common commercially-available metal powders or metal halides, if there have been no problems with storage and handling before use. This is because most water contents are 1% or less. Even if drying is performed, it is not necessary to use special equipment such as that for vacuum drying. Subsequently, the materials

are weighed in the prescribed weight ratios, and are introduced into a mill and milled and mixed.

The milling device used in this case is preferably a ball mill, rod mill or other milling device that uses a milling medium. This is because [such mills] have grinding actions. After milling, the metal halide treated metal powder is removed and used without the need for additional post-processes such as drying. Consequently, with the present invention, production is extremely simple in contrast to other production methods for deoxygenation agents.

With the deoxygenation agent obtained in this manner, in contrast to simple mixing methods or aqueous solution treatment methods, the fine metal halide, which has fresh surfaces is affixed to metal powder surfaces generated by milling, which are likewise fresh, and thus [the metal halide] is extremely firmly bound; and there is no loss of the metal halide even when the metal halide treated metal powder is packaged to produce a deoxygenation agent, so that stable deoxygenation performance is achieved.

The deoxygenation agent produced by the present invention does not itself have a water content, and so is stable and does not undergo deoxygenation reactions in atmospheres having low moisture content, but when the moisture content increases, the metal halide on the metal surfaces deliquesces, and reacts at a high reaction rate with oxygen in the air.

Consequently, by sealing the deoxygenation agent of the present invention in packaging material that is not air permeable along with food containing water, the oxygen concentration in the packaging material decrease with passage of time and eventually becomes zero.

(Embodiment 1)

Reduced iron powder, pure iron powder and cast iron powder were used as the metal powder, and 1 kg of starting material was prepared by adding 1% NaCl as the metal halide. This starting material was milled and mixed for 60 min in a vibration mill with a container volume of 3.59 L

at an amplitude of 5 mm after introducing three SC steel rods with diameters of 30 mm and lengths of 210 mm.

For purposes of comparison with the deoxygenation agent produced in this manner, metal halide powders were prepared by a conventional technology by mixing 2 mL of 10% NaCl aqueous solution with 20 g of the same three types of iron powder as above, followed by vacuum drying at a temperature of about 100°C.

These treated powders in the amount of 5 g were introduced into paper pouches laminated with 35 x 45 mm porous polyethylene films, thus producing deoxygenation agents. These were then sealed in 100 cc sealed containers, which were controlled at relative humidities of no less than 90% and no greater 50%. Subsequently, the oxygen concentrations in the containers were measured over time. The measurement temperature was controlled at $20 \pm 1^\circ\text{C}$.

The results are presented in Table 1.

The deoxygenation agent of the present invention exhibited favorable performance relative to the comparative materials, in that the oxygen concentration in the container reached 0% within a maximum period of 25 hours, even at a relative humidity of 90% or greater. In particular, the most desirable results were exhibited when reduced iron powder was used.

At a relative humidity of 50% or less, the maximum oxygen absorption amount over a period of 25 hours reached no more than 3%, for a total content of about 14%. Thus, it was found that there was almost no reaction at lower moisture content, and it was found that the desired performance as a deoxygenation agent was present.

(Embodiment 2)

Reduced iron powder and dry powder of cast iron material corresponding to FC₂₀ was used as the metal powder, and 1% NaCl was added thereto as the metal halide. This raw material was introduced, in the amount of 1 Kg, together with three SC steel rods with diameters of 30 mm and lengths of 210 mm into a vibration mill with a vibration frequency of 1200 cpm, an amplitude of 5 mm and a container volume of 3.59 L. With reduced iron, milling and mixing were carried out for 60 min, and with the dry powder, milling and mixing were carried out for 60 min and for 120 min.

These metal halide treated iron powders, in the amount of 5 g, were sealed in 35 x 45 mm paper pouches laminated with porous polyethylene film to produce deoxygenation agents. These were sealed in a sealed container with a volume of 100 cc controlled so that the relative humidity was 90% or greater. The measurement temperature was maintained at $20 \pm 1^\circ\text{C}$. The results of measuring the oxygen concentration in the container over time are presented in Table 2.

Table 3 shows the particle size of the reduced iron and dry powder prior to milling, and although the dry powder particle size was coarse in comparison to the

reduced iron powder, the performance of the resulting deoxygenation agent was the closest to reduced iron powder which had the most favorable performance in comparison to the other raw material powders shown in Table 1.

In addition, the metal halide treated dry powder was easy to handle because it was dry without being tacky. This is thought to result from the graphite in the cast iron which serves to regulate water content and also acts to retain the metal halide powder.

It is a characteristic of the present invention that it is possible to improve deoxygenation performance by appropriately adjusting the milling parameters, even with coarse metal powders.

(Embodiment 3)

Three types of metal powders, namely, reduced iron powder, pure iron powder and cast iron powder, were prepared as in Embodiment 1, and NaCl and CaCl₂ were added at 0.1, 0.5, 1, 5 and 10% as the metal halides.

These materials were used in order to prepare metal halide treated iron powders using different milling and mixing times of 60 min, 90 min, 120 min and 200 min in the same vibration mill as in Embodiment 1.

These iron powders, in the amount of 5 g, were sealed in paper pouches laminated with a porous polyethylene film with inner dimensions of 45 x 35 mm, thus producing deoxygenation agents. These were then placed in a container with a volume of 100 cc at a relative humidity of 90% or greater in the same manner as in Embodiment 1, and the change in oxygen level over time was measured at a temperature of $20 \pm 1^\circ\text{C}$.

Table 4 shows the time required for the oxygen concentration to reach 0% and the change in oxygen concentration over time in the container.

From these results, it was found that the use of NaCl provides superior oxygen absorption capacity as compared to when CaCl₂ is used as the metal halide. In terms of the influence of NaCl concentration, no great change in performance was seen between 0.5 and 10%, although a significant decrease in performance occurred when the value decreased to 0.1%.

In addition, with 10% NaCl, bleeding into the packaging paper was seen with the deoxygenation agents in which pure iron or reduced iron powder was used, but this was not seen with cast iron powder. This is a characteristic of cast iron powder that is thought to result from the same reasons as described

in Embodiment 2.

From these results, suitable NaCl concentrations are preferably 0.5 to 5%, in consideration of bleeding problems, performance, and economics.

In addition, the changes in performance were observed when 1% was used for the NaCl addition concentration, and the milling time was varied, and the performance was improved when the milling time was lengthened to 120 min. No great improvement in effects was seen when the milling time was further increased. This is thought to be because the metal halide is made finer as the milling time is lengthened, and adheres tightly to the surfaces of the metal powder.

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Table 1

| | Relative humidity (%) | Deoxidation agent form | | | Oxygen concentration in container (%) | | | | Time to reach 0% oxygen concentration(h) |
|---------------------------------|-----------------------|------------------------|------------------|---|---------------------------------------|------|------|------|--|
| | | Metal powder | Metal halide (%) | | 10 | 15 | 20 | 25 | |
| Method of the present invention | >90 | Reduced iron powder | NaCl | 1 | 1.4 | 0.03 | 0 | 0 | 19 |
| | | Pure iron powder | NaCl | 1 | 13.8 | 7.6 | 3.1 | 0 | 23 |
| | | Cast iron powder | NaCl | 1 | 10.7 | 5.0 | 2.5 | 0 | 25 |
| | <50 | Reduced iron powder | NaCl | 1 | 20.1 | 18.7 | 18.0 | 18.0 | - |
| | | Pure iron powder | NaCl | 1 | 20.8 | 20.7 | 20.6 | 20.3 | - |
| | | Cast iron powder | NaCl | 1 | 20.0 | 19.0 | 18.0 | 17.7 | - |
| Conventional method | >90 | Reduced iron powder | NaCl | 1 | 14.8 | 8.9 | 4.1 | 0 | 25 |
| | | Pure iron powder | NaCl | 1 | 14.2 | 8.1 | 3.5 | 0 | 24 |
| | | Cast iron powder | NaCl | 1 | 14.1 | 10.1 | 6.8 | 4.3 | 32 |
| | <50 | Reduced iron powder | NaCl | 1 | 20.0 | 19.0 | 18.0 | 18.0 | - |
| | | Pure iron powder | NaCl | 1 | 19.8 | 19.2 | 19.0 | 19.0 | - |
| | | Cast iron powder | NaCl | 1 | 20.5 | 20.0 | 19.0 | 19.0 | - |

Table 2

| Deoxidation agent production conditions | | | | Oxygen concentration in container (%) | | | | Time to reach 0% oxygen concentration (h) |
|---|--------------|-------------------|------------------|---------------------------------------|------|------|------|---|
| Metal powder | Metal halide | Concentration (%) | Milling time (%) | 10 h | 15 h | 20 h | 25 h | |
| Reduced iron powder | NaCl | 1 | 60 | 1.4 | 0.03 | 0 | 0 | 19 |
| Dry powder | NaCl | 1 | 60 | 5.8 | 2.0 | 0.3 | 0 | 22 |
| Dry powder | NaCl | 1 | 120 | 2.5 | 0.1 | 0 | 0 | 20 |

Table 3

| | (wt%) | | | | | | |
|--------------|-------|-----|------|------|------|-----|------|
| Mesh | +60 | 100 | 150 | 200 | 270 | 325 | -325 |
| Reduced iron | 0.1 | 1.1 | 15.7 | 16.6 | 13.8 | 6.8 | 45.9 |
| Dry powder | 84.4 | 8.4 | 2.9 | 3.5 | 0.4 | 0.2 | 0.2 |

Table 4

| Deoxidation agent production conditions | | | | Oxygen concentration in container (%) | | | | Time to reach 0% oxygen concentration (h) |
|---|-------------------|-------------------|------------------|---------------------------------------|------|------|------|---|
| Metal powder | Metal halide | Concentration (%) | Milling time (%) | 10 h | 15 h | 20 h | 25 h | |
| Reduced iron powder | NaCl | 0.1 | 60 | 10.3 | 8.5 | 7.0 | 3.0 | 30 |
| | | 0.5 | 60 | 2.4 | 1.0 | 0.1 | 0 | 21 |
| | | 1 | 60 | 1.4 | 0.03 | 0 | 0 | 19 |
| | | 1 | 90 | 1.3 | 0.02 | 0 | 0 | 17 |
| | | 1 | 120 | 1.0 | 0.01 | 0 | 0 | 16 |
| | | 1 | 200 | 0.8 | 0.01 | 0 | 0 | 16 |
| | | 5 | 60 | 1.9 | 1.0 | 0 | 0 | 20 |
| | | 10 | 60 | 1.5 | 0.5 | 0 | 0 | 20 |
| | CaCl ₂ | 1 | 60 | 16.2 | 10.5 | 4.8 | 1.7 | 28 |
| | | | | | | | | |
| Pure iron powder | NaCl | 0.1 | 60 | 19.2 | 14.3 | 7.0 | 3.5 | 32 |
| | | 0.5 | 60 | 11.0 | 6.2 | 2.6 | 0 | 25 |
| | | 1 | 60 | 13.8 | 7.6 | 3.1 | 0 | 23 |
| | | 1 | 90 | 10.0 | 6.0 | 2.5 | 0 | 21 |
| | | 1 | 120 | 10. | 5.2 | 2.1 | 0 | 20 |
| | | 1 | 200 | 9.8 | 5.3 | 2.2 | 0 | 20 |
| | | 5 | 60 | 10.3 | 5.9 | 2.5 | 0 | 21 |
| | | 10 | 60 | 11.2 | 6.1 | 2.9 | 0 | 22 |
| | CaCl ₂ | 1 | 60 | 17.2 | 10.8 | 5.0 | 3.0 | 29 |
| | | | | | | | | |
| Cast iron powder | NaCl | 0.1 | 60 | 12.4 | 8.8 | 6.3 | 4.1 | 31 |
| | | 0.5 | 60 | 11.0 | 6.3 | 2.8 | 0.05 | 26 |
| | | 1 | 60 | 10.7 | 5.0 | 2.5 | 0 | 25 |
| | | 1 | 90 | 11.0 | 4.3 | 1.0 | 0 | 22 |
| | | 1 | 120 | 9.8 | 4.0 | 0.8 | 0 | 20 |
| | | 1 | 200 | 9.5 | 4.1 | 0.8 | 0 | 20 |
| | | 5 | 60 | 10.0 | 4.2 | 0.9 | 0 | 21 |
| | | 10 | 60 | 9.8 | 4.2 | 0.8 | 0 | 20 |
| | CaCl ₂ | 1 | 60 | 15.8 | 10.2 | 5.1 | 3.2 | 30 |
| | | | | | | | | |

(Effect of the Invention)

The deoxygenation agent produced by means of the present invention has stable performance with a simple production method, while also having superior oxygen absorption capacity as compared to conventional methods. Moreover, the method is also characterized in that, in addition to costly iron powder, materials can be used as the metal powder that have traditionally been regarded as waste materials, such as dry powder or particulate iron generated during iron production which is preliminarily crushed to generate cracking; and by adjusting the milling conditions with the metal halide, it is possible to produce a deoxygenation agent having a performance that is equivalent to or better than iron powder.

Consequently, the present invention has extremely high practical value.

4. Brief Description of the Drawings

Fig. 1 is a schematic block diagram of the production process for deoxygenation agents according to the present invention; and Fig. 2 is a graph showing the relationship between the amount of salt added, the time required for the oxygen concentration to reach zero and deoxygenation initiation time.

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FIG. 1

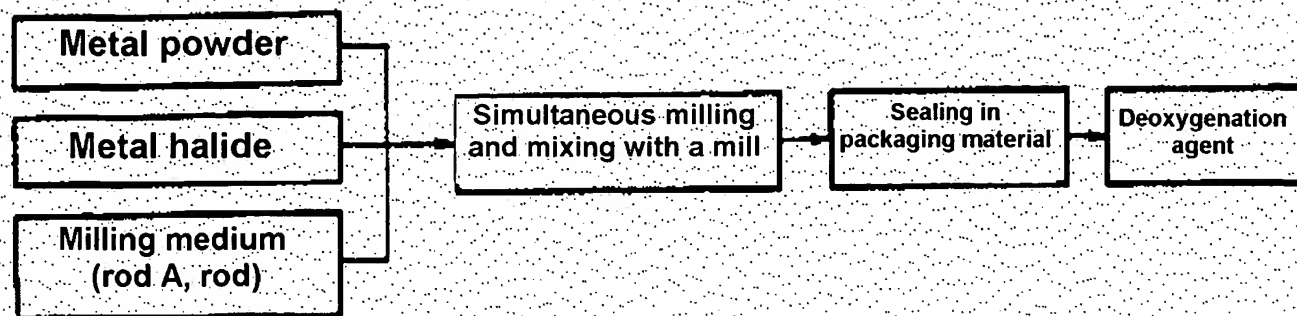


FIG. 2

